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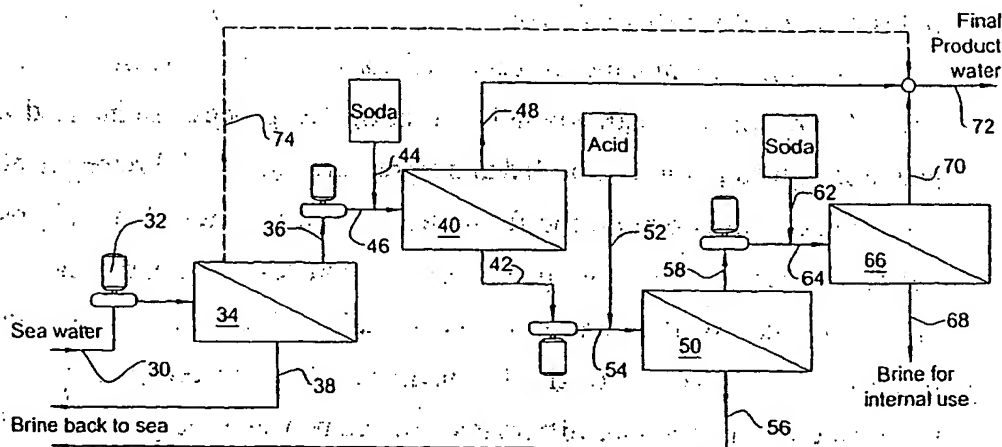
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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF BORON REMOVAL IN PRESENCE OF MAGNESIUM IONS



(57) Abstract: A method of boron removal from saline water containing boron and magnesium salts including a multi-stage reverse-osmosis (RO) separation process and comprising the steps of a first stage RO separation at pH < 8.2; a second stage RO separation over at least part of the first-stage permeate; a third stage RO separation over the second-stage brine. The method is characterized in that the second stage separation is carried at pH > 9 and the brine concentration is limited to a degree preventing Mg(OH)₂ scaling on RO membrane surfaces, the permeate constitutes product water, and the brine contains boron and magnesium ions; the third stage separation is carried at weak-acid pH, whereby the bulk of said magnesium ions are separated with the brine, while the bulk of said boron ions are retained in the permeate. The method further comprises a fourth stage of separation over the third-stage permeate, where the bulk of said boron ions is separated from said third-stage permeate, and the permeate of the fourth stage constitutes product water with low boron content.

METHOD OF BORON REMOVAL IN PRESENCE OF MAGNESIUM IONS

FIELD OF THE INVENTION

This invention relates to methods of water desalination and in particular to methods of boron ion removal from water containing magnesium salts.

BACKGROUND OF THE INVENTION

5 Desalination is a separation process used to reduce the dissolved salt content of saline water to a usable level. The saline feedwater is drawn from the sea or from underground sources (brackish water). The desalination process separates it into two output streams: low-salinity product water and very saline concentrate stream (brine or reject water). The product water of the desalination
10 process is generally water with less than 0.5 g/L or 500 ppm TDS (Total Dissolved Solids), which is suitable for most domestic, industrial, and agricultural uses. A by-product of desalination is brine, which is a concentrated salt solution and is usually disposed of.

A typical membrane process used for desalination is the reverse osmosis
15 (RO). As shown schematically in Fig. 1, in the RO process, saline feedwater 10 is pressurized by a pump 12 and fed into a pressure vessel 14. Pretreatment agent 16 may be added to condition the feedwater. RO membranes 18 are disposed in the vessel 14 across the flow path. The membranes 18 inhibit the passage of dissolved salts while permitting the desalinated product water (also called
20 permeate) 20 to pass through. The permeate 20 is forced to flow through the membrane by the pressure differential created between the pressurized feedwater and the product water, which is at near-atmospheric pressure. Because no membrane is perfect in its rejection of dissolved salts, a small percentage of salt passes through the membrane and remains in the product water. The remaining

feedwater is discharged through the pressurized side of the pressure vessel as brine 22.

Boron is contained in seawater in a typical concentration of about 4-5 ppm. In one RO desalination stage, its concentration is lowered to 1-1.5 ppm, which is tolerated by humans. Some agricultural crops, however, are troubled with boron toxicity at low levels. For example, California standard for irrigation water is a maximum of 0.75 mg/L (0.75 ppm). In Israel, where the desalinated water is used in a unified system both for potable water and for irrigation, requirements to boron content are even more rigorous - 0.2 ppm (0.2 mg/L).
10 Some industrial applications, such as the manufacture of electronic parts, speciality foods, and pharmaceuticals, also require very low concentration of boron in water.

At present, such standards can only be met by the use of costly ion exchange resins. Membrane systems have failed to perform effectively due to
15 scaling problems or insufficiently high rejection rates for boron. The above described reverse osmosis method allows to remove only 60% to 80% of boron ions, while the other ions are removed by more than 99%, usually 99.6%.

The RO membranes have low effect in separating boron ions at $\text{pH} < 9$. This fact is due to some peculiarities in the dissociation of various boric acid
20 forms in seawater. It is known that boron ions rejection by reverse osmosis membranes increases with increasing feedwater pH. However, seawater desalination by the RO method is not practical at $\text{pH} > 9$ due to the crystallization of CaCO_3 and $\text{Mg}(\text{OH})_2$ salts on the RO membranes (fouling).

The improvement of the RO membrane method for removing the boron
25 ion from desalinated seawater has been addressed by a number of inventors. Prior art JP 11138165 suggests treatment of the feed water with antiscaling agent before RO processing at $\text{pH} = 9.2$. US 5250185 suggests removal of all bivalent cations (such as Mg^{++}) from feed water by treatment with water softener prior to RO process at $\text{pH} > 9.5$. US 5925255 suggests removal of hardness and
30 non-hydroxide alkalinity from feed water in a weak acid cation ion exchange resin, then RO processing at $\text{pH} > 10.5$.

Suggestions have been made to remove the boron ions before the RO treatment. JP 09220564 suggests adding a flocculant to feed water, forming boron-containing insoluble precipitate, and microfiltering. Similarly, JP 10225682 suggests adding a coagulant for the same purpose. JP 10080684 suggests adding sodium fluoride to boron-containing feed water in order to form a complex, which is then rejected by a RO membrane.

According to other suggestions, boron ions are removed after the RO desalination. JP 11128922 suggests treating the boron-containing permeate in one or two positively charged RO membranes. JP 11128923 removes the boron ion in a series of RO membranes. JP 10015356, JP 10085743, and JP 11128924 use various types of ion exchange devices after the RO membrane. However, this group of inventions does not address the membrane scaling at high pH.

Still other suggestions deal with processes with two or more stages of RO for successive removal of scaling salts and boron ions. JP 59213489 suggests adding chlorine agent to boron-containing feedwater, and a first-stage RO treatment through chlorine-resistant membrane to remove inorganic and organic salts, Ca and Mg salt, and a part of boron. Then the permeate undergoes a second stage separation by a permeable membrane having an N-identical bond in the -CONH- molecule. JP 9290275 suggests removing polyvalent cations in a first stage RO device, then raising the alkalinity of the permeate to $\text{pH} \geq 9$ by adding lime and removing boron in a second stage RO device. JP 8206460 combines a first stage low-pressure RO unit separating polyvalent ions (scale components) and a second high-pressure RO unit for deep separation of boron. Both stages work at $\text{pH} = 6.5$. JP 11010146 suggests a two-stage RO separation at neutral pH, where the first stage permeate is collected in two flows, a first one from the high-pressure feed side of the pressure vessel, and a second one from the brine discharge side. The second flow is passed through a second stage RO and then the second stage permeate is mixed with the first flow.

JP 11267645 discloses a two-stage RO desalination method. The boron containing feed water is acidified, deaerated, and passed through a first stage RO device. Then the water is conditioned to $\text{pH} \geq 9.2$ and treated in a second stage RO device.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a method of deep boron removal from water containing boron and magnesium salts in a multi-stage reverse-osmosis (RO) separation process. The method comprises: a first stage RO separation at $\text{pH} < 8.2$; a second stage RO separation over the first-stage permeate at $\text{pH} > 9$, wherein the brine concentration is limited to a degree preventing $\text{Mg}(\text{OH})_2$ scaling on RO membrane surfaces, the permeate constituting product water, and the brine containing boron and magnesium ions; a third stage RO separation over the second-stage brine at weak-acid pH, wherein the bulk of the magnesium ions are separated with the brine, while the bulk of the boron ions are retained in the permeate; and a fourth stage RO separation over the third-stage permeate at $\text{pH} > 9$, wherein the bulk of the boron ions is separated with the brine, and the permeate constitutes product water with low boron content.

A part of the permeate at the first separation stage may be collected from RO membranes at the upstream side of the RO vessel (front permeate). This part has lower concentration of boron than the rest of the permeate, and may be used for obtaining final product water by mixing with the product water from the second and the fourth stage. The collection of front permeate provides for an effective way to maintain the concentration of boron in the final product water at a predetermined level under variable temperature of the entrant saline feedwater: the rate of collection is reduced at higher feedwater temperature.

The proposed multi-stage desalination and boron removal method provides the benefits of:

- high product yield, about 98% of the second stage feedwater flow,
- low specific power consumption since almost all entrant water passes the boron removal stages and is transformed into product water, with less than 2% being rejected;
- low consumption of chemicals, since acidifying and CO_2 removal from the first stage feedwater may be skipped, as far as the second stage

operates at low brine concentration, and $\text{Mg}(\text{OH})_2$ and CaCO_3 scaling does not occur;

- low capital investment when both low boron content and low TDS content are required in the product water; and
- 5 - flexibility and easy adjustment to changes of the feedwater temperature.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to understand the invention and to see how it may be carried out in practice, an embodiment will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

Fig. 1 is a schematic layout of a typical reverse osmosis pressure vessel.

Fig. 2 is a schematic layout of a multi-stage desalination plant for boron removal according to the method of the present invention.

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DETAILED DESCRIPTION OF THE INVENTION

A the method of the present invention implemented in a four-stage seawater desalination plant is illustrated in Fig. 2. Feedwater 30, taken from the sea, is pressurized by a high-pressure pump 32 and is fed into the pressure vessel of the first stage 34 for reverse-osmosis separation into permeate 36 and brine 38. 20 The first stage desalination is done in the standard way at $\text{pH} < 8.2$. However, acidifying of the feedwater and CO_2 removal before the first stage may be omitted because the second stage operates with low brine concentration, as will be explained below.

25 Desalinated water obtained as first-stage permeate 36 contains about 1-1.5 ppm boron ions and a certain quantity of Mg^{++} ions. The rest of ions contained in the first stage permeate play a less significant role in the process and will not be discussed further. The presence of magnesium ions does not allow to achieve, in one desalination stage, high $\text{pH} > 9$ and high brine concentration,

since those conditions lead to intensive crystallization of $\text{Mg}(\text{OH})_2$ on the membrane surface.

According to the present invention, in the second stage pressure vessel 40, the desalination is carried at $\text{pH} > 9$ but the brine 42 is concentrated to a degree lower than the saturation level, thus preventing the scaling (crystallizing) $\text{Mg}(\text{OH})_2$ on membranes' surface. The brine concentration in this stage does not exceed 70-85%. The higher pH at the second stage may be achieved by adding soda 44 to the feedwater 46 or by any other means. The second stage permeate 48 has a low concentration of boron ions and constitutes product water.

The second stage of desalination may be defined as a stage of high pH and low brine concentration. The brine 42 discharged from the second stage is about 15-30% of the originally desalinated seawater volume. It has a high concentration of boron and magnesium ions.

According to the present invention, the second stage brine 42 is processed in the third stage RO pressure vessel 50 at low pH values. For this purpose, before the third stage, acid 52 is added to the feedwater 54 so as to reduce its pH to about 6. Due to the low pH value, the Mg^{++} cations cannot cause crystallization of $\text{Mg}(\text{OH})_2$ on the membrane surface even at a very high concentration and are rejected with the third stage brine 56. For the same reason of low pH, the boron ions are only weakly rejected and remain with the third stage permeate 58. Accordingly, the third stage of desalination may be defined as a stage of low pH and high brine concentration.

The third stage permeate 58 retains high concentration of boron ions and cannot be used as product water. However, it does not contain magnesium cations. This combination of concentrated boron ions and absence of magnesium cations allows further desalination to be carried out at high values of $\text{pH} > 9$. The permeate 58 is treated with soda 62 for raising its pH, and is supplied as feedwater 64 to the fourth stage RO pressure vessel 66. In the fourth stage, high yield of product water 70 is obtained. As the permeate 58 from the third stage has very low TDS, the fourth stage brine has a relatively low TDS content and may be used for the desalination plant internal needs such as membrane flushing and

cleaning. The fourth stage of desalination may be defined as a stage of high pH and high yield.

The fourth stage permeate 70 has a low concentration of boron ions and constitutes an output product. It may be mixed with the second stage permeate 48 to obtain final product water 72 with specified salt concentration.

The entrant seawater temperature affects the degree of boron rejection at the RO membranes and the saturation concentration at which $Mg(OH)_2$ starts to form scale on the RO membranes. The scheme of boron removal in accordance with the present invention advantageously provides a flexible method to maintain a specified boron concentration in the output product at minimal energy consumption. In accordance with this method, a part of the first stage permeate 36 is collected from the high-pressure feed side of the RO vessel 34. This is the so-called front permeate 74 containing about 3 times lesser concentration of boron than the remaining permeate 36. This concentration is still higher than the desired concentration in the output product, but the front permeate 74, when mixed with the second stage permeate 48 and the fourth stage permeate 70, may provide for the specified boron concentration in the final product water 72. The maintenance of the boron concentration is performed by regulating the flow of front permeate 74. At high temperature the flow of front permeate is reduced while at low temperature the flow is increased.

The peculiarities in the design of the second, third, and fourth desalination stages lie in the choice of materials resistant to high or low pH values. The second and the fourth stage components, such as high-pressure pipes, seals, membranes, valves must endure $pH > 9$ without corrosion, while the elements of the third stage must endure $pH < 6$.

Although a description of a specific embodiment of the method of the present invention has been presented, it is contemplated that various changes could be made without deviating from the scope of the invention. For example, treatment stages for other purposes may be introduced before, after or in-between the shown RO stages. The method may be used for purification of brackish waters or other boron-contaminated water.

CLAIMS:

1. A method of boron removal from saline water containing boron and magnesium salts including a multi-stage reverse-osmosis (RO) separation process yielding product water, each stage of said process being carried out in a pressurized vessel with RO membranes separating entrant saline feed water into permeate with low salt concentration and brine with high salt concentration, said method comprising at least the steps of:

- a first stage RO separation at $\text{pH} < 8.2$;
 - a second stage RO separation over at least part of the first-stage permeate;
 - a third stage RO separation over the second-stage brine;
- characterized in that

the second stage separation is carried at $\text{pH} > 9$ and the brine concentration is limited to a degree preventing $\text{Mg}(\text{OH})_2$ scaling on RO membrane surfaces, the permeate constituting product water, and the brine containing boron and magnesium ions;

the third stage separation is carried at weak-acid pH, whereby the bulk of said magnesium ions are separated with the brine, while the bulk of said boron ions are retained in the permeate, wherein

the method further comprises a fourth stage of separation over the third-stage permeate, where the bulk of said boron ions is separated from said third-stage permeate, and the permeate of the fourth stage constitutes product water with low boron content.

2. The method of Claim 1, wherein final product water with predetermined low boron concentration is obtained by mixing said product water from the second stage and said product water from the fourth stage.

3. The method of Claim 1, wherein a part of the permeate at said first RO separation stage is used for obtaining final product water by mixing with said product water from the second stage and/or said product water from the fourth

stage, said part of the permeate being collected from membranes at the upstream side of the RO vessel (front permeate) and having lower concentration of boron than the rest of the permeate.

5 4. The method of Claim 3, wherein the concentration of boron in the final product water is maintained at a predetermined level by regulating the collection of said front permeate in dependence on the entrant saline feedwater temperature, reducing the rate of said collection at higher feedwater temperature.

10 5. The method of Claim 1, wherein said fourth stage separation is carried in a pressurized vessel with RO membranes at $\text{pH} > 9$.

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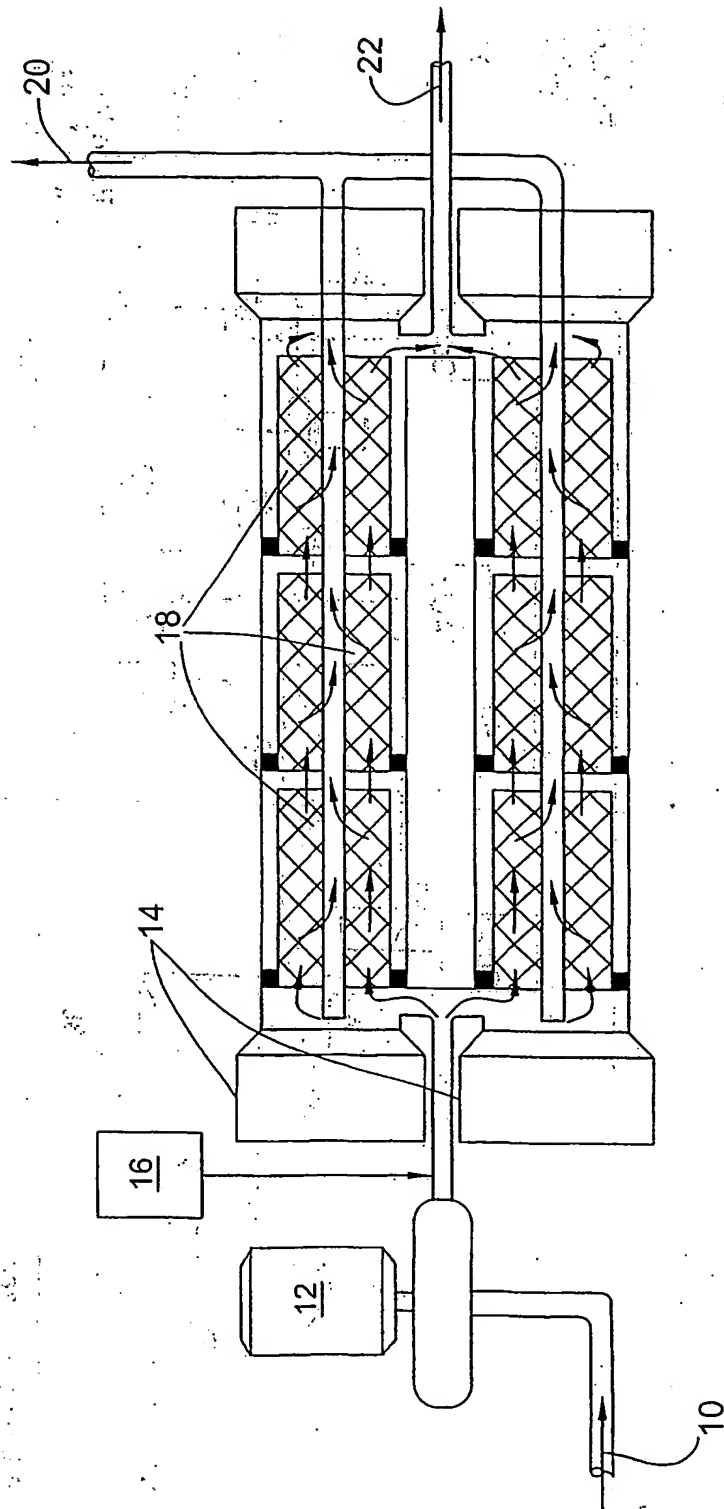


FIG. 1

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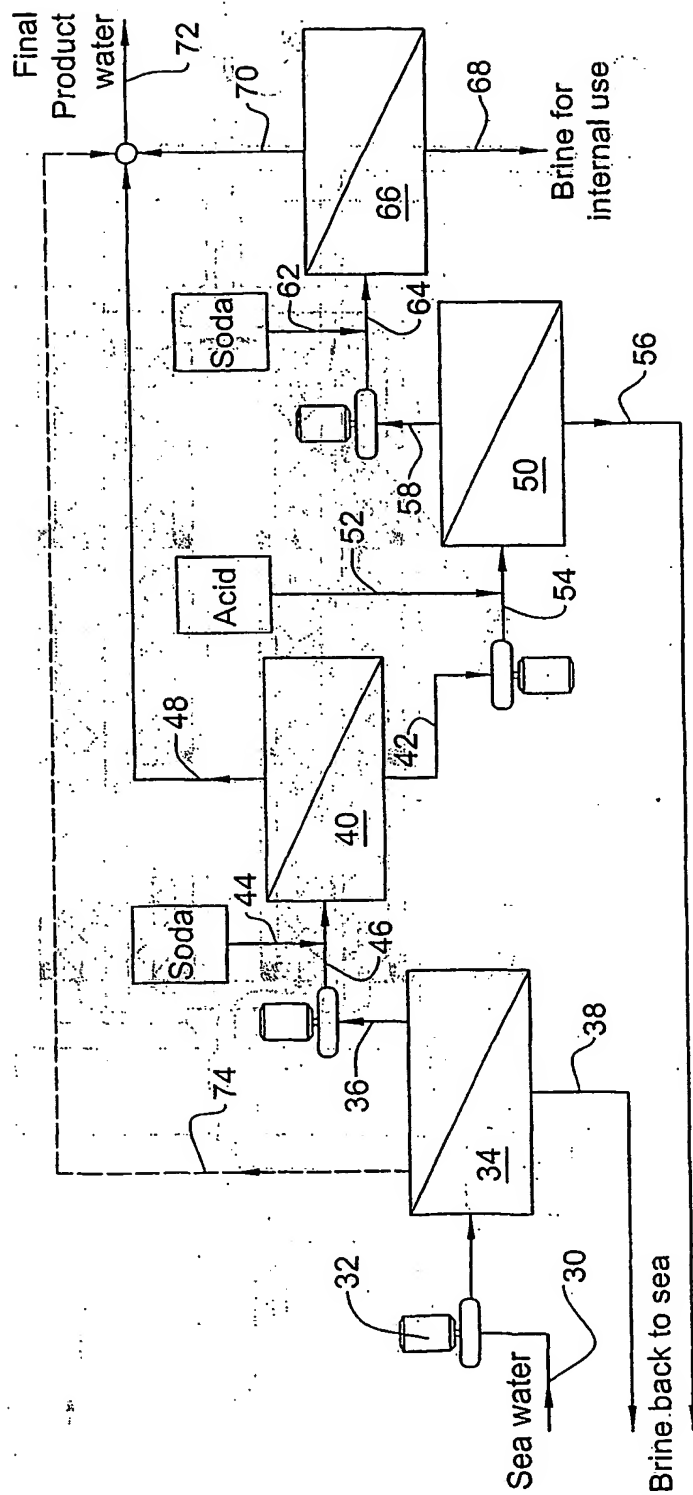


FIG. 2

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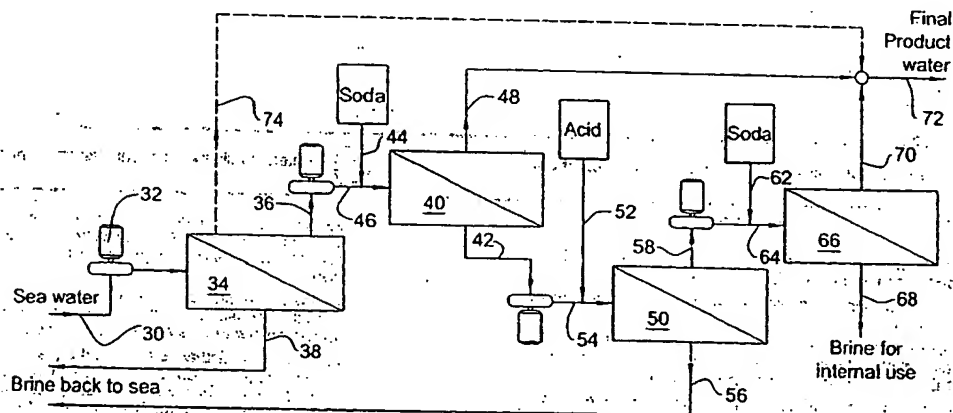
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(54) Title: METHOD OF BORON REMOVAL IN PRESENCE OF MAGNESIUM IONS



(57) Abstract: A method of boron removal from saline water containing boron and magnesium salts including a multi-stage reverse-osmosis (RO) separation process and comprising the steps of a first stage RO separation (34) at pH < 8.2; a second stage RO separation (40) over at least part of the first-stage permeate (36); a third stage RO separation (50) over the second-stage brine (42). The method is characterized in that the second stage separation (40) is carried at pH > 9 and the brine (42) concentration is limited to a degree preventing Mg(OH)₂-scaling on RO membrane surfaces, the permeate (48) constitutes product water, and the brine (42) contains boron and magnesium ions; the third stage separation (50) is carried at weak-acid pH, whereby the bulk of said magnesium ions are separated with the brine (56), while the bulk of said boron ions are retained in the permeate (58). The method further comprises a fourth stage of separation (66) over the third-stage permeate (58), where the bulk of said boron ions is separated from said third-stage permeate (58), and the permeate (70) of the fourth stage (66) constitutes product water with low boron content.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, EPO-Internal, WPI Data, CHEM ABS Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 1996, no. 12, 26 December 1996 (1996-12-26) -& JP 08 206460 A (TORAY IND INC), 13 August 1996 (1996-08-13) cited in the application abstract; figures 2,5 paragraphs '0001!', '0011!', '0013!', '0014!', '0016!'-'0018!', '0020!', '0039!', '0051!', '0052!', '0058!', '0064!' -& DATABASE WPI Derwent Publications Ltd., London, GB; AN 1996-420279 XP002213760 -& JP 08 206460 A abstract</p> <p style="text-align: center;">-/-</p>	1



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Date of the actual completion of the international search

17 September 2002

Date of mailing of the international search report

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Int. Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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